#### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

# (19) World Intellectual Property Organization International Bureau





### (43) International Publication Date 1 May 2003 (01.05.2003)

## **PCT**

# (10) International Publication Number WO 03/035714 A1

(51) International Patent Classification7: C08G 61/12, C07D 333/20

Madingley Rise, Cambridge, Cambridgeshire CB3 OTX (GB).

- (21) International Application Number: PCT/GB02/04723
- (22) International Filing Date: 18 October 2002 (18.10.2002)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 0125620.5

25 October 2001 (25.10.2001) GH

- (71) Applicant (for all designated States except US): CAM-BRIDGE DISPLAY TECHNOLOGY LIMITED [GB/GB]; Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): TOWNS, Carl [GB/GB]; Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB). MCKIERNAN, Mary [GB/GB]; Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 OTX (GB). O'DELL, Richard [GB/GB]; Cambridge Display Technology Limited, Greenwich House, Madingley Road,

- (74) Agent: SHADE, Matthew; Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TRIARYLAMINE CONTAINING MONOMERS FOR OPTOELECTRONIC DEVICES

(57) Abstract: Monomers having the formula X1-Ar1-[triarylamine]-Ar2-X2 wherein the triarylamine unit comprises at least one nitrogen atom in the backbone of the monomer and at least three substituted or unsubstituted aryl or heteroaryl groups and wherein X1 and X2 are the same or different polymerisable groups and wherein Ar1 and Ar2 are the same or different substituted or unsubstituted aryl or heteroaryl groups. Polymers and copolymers comprising such monomers are also described. The polymers have particular application in organic optoelectronic devices such as organic electroluminescent devices and organic photovoltaic devices.



TRIARYLAMINE CONTAINING MONOMERS FOR OPTOELECTRONIC DEVICES

The present invention relates to triarylamine based trimer monomers and to low band gap polymers and copolymers prepared therefrom and in particular to optoelectronic devices such as electroluminescent devices and photovoltaic devices comprising such polymers and copolymers.

## **Background of the Invention**

Semiconductive organic polymers have been known for several decades, during the past ten years they have seen increasing application in the field of electroluminescent devices, see for example WO90/13148. A typical electroluminescent device comprises an anode, a cathode and a layer of light-emitting material situated between the anode and the cathode, further layers may also be introduced to improve charge injection into the device or charge transport through the device. Semiconductive organic polymers may act as the light-emitting component or as charge transport or charge injecting components in electroluminescent devices. More recently semiconductive organic polymers have found application in photovoltaic devices, as disclosed in WO96/16449, and also as photoconductors and photodetectors.

The nature of the polymeric material used in electroluminescent devices is critical to the performance of the device, materials used include poly(phenylenevinylenes), as disclosed in WO90/13148, polyfluorenes, as disclosed in WO97/05184, poly(arylamines), as disclosed in WO98/06773. In particular copolymers and blends of polymers have been found to be useful in such devices, as disclosed in WO92/03490, WO99/54385, WO00/55927 and WO99/48160. Poly(arylamines) have been disclosed in which the aromatic groups may comprise heteroaromatic moieties such as triazine, see WO01/49769.

Recently there have been efforts to increase the range of available semiconductive polymers and, in particular, to provide polymers with lower band gaps, see WO01/49768. The band gap is the difference in energy levels between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Low band gap materials emit light at longer wavelengths i.e. towards the red

end of the visible region of the electromagnetic spectrum and are also promising candidates for polymeric photovoltaic devices. WO01/49768 discloses a range of low band gap polymers comprising heterocyclic moleties such as benzothiadiazole. Benzothiadiazole is a functional group characterised by its light-emitting and electron transporting properties.

## Summary of the Invention

It is an object of the present invention to provide a range of low band gap polymers and copolymers which give efficient emission of light and have utility as hole-transporting components in optoelectronic devices. The invention provides a range of monomers which may be polymerised to provide low band gap polymers and copolymers, the invention further provides optoelectronic devices comprising said polymers and copolymers and methods for the polymerisation of said monomers.

In a first embodiment the present invention provides monomers having the formula

X<sub>1</sub>-Ar<sub>1</sub>-[triarylamine]-Ar<sub>2</sub>-X<sub>2</sub>

wherein the triarylamine unit comprises at least one nitrogen atom in the backbone of the monomer and at least three substituted or unsubstituted aryl or heteroaryl groups, said groups being the same or different,

wherein X<sub>1</sub> and X<sub>2</sub> are the same or different polymerisable groups,

wherein  $Ar_1$  and  $Ar_2$  are the same or different substituted or unsubstituted aryl or heteroaryl groups.

For the purpose of the present invention the term the backbone of the monomer is taken to mean that linear chain to which all other chains may be regarded as being pendant, i.e. that part of the monomer which will be situated in the backbone of the eventual polymer. The backbone is sometimes also referred to as the main chain.

In a more preferred embodiment groups  $Ar_1$  and  $Ar_2$  are heteroaromatic groups such as thiophene, pyrrole, furan or pyridine, thiophene is particularly preferred. Polymerisable groups  $X_1$  and  $X_2$  are preferably selected from the group comprising Cl, Br, I, boronic acids, boronic esters or boranes. In a preferred embodiment polymerisable groups  $X_1$  and  $X_2$  are selected from the group comprising Br and boronic esters.

The groups  $Ar_1$  and  $Ar_2$  may be substituted with moleties selected from the group comprising aryl, alkyl, cycloalkyl and alkoxy.

The triarylamine group may comprise a heteroaryl group, this may be either in the chain of the monomer or pendant to the monomer, examples of heteroaryl groups are pyridine, and triazine. In a preferred embodiment the triarylamine comprises a triazine group. The triarylamine group comprises at least one nitrogen, in preferred embodiments the triarylamine group comprises one or two nitrogens.

Particularly preferred monomers are those having the structural formula

$$X_1$$
— $Ar_1$ — $Ar_3$ — $N$ — $Ar_5$ — $Ar_2$ — $X_2$ 
 $Ar_4$ 

wherein  $X_1$  and  $X_2$  are the same or different polymerisable groups and wherein  $Ar_1$ ,  $Ar_2$ ,  $Ar_3$ ,  $Ar_4$  and  $Ar_5$  are the same or different substituted or unsubstituted aryl or heteroaryl groups. Or those monomers having the structural formula

$$X_1$$
— $Ar_1$ — $Ar_6$ — $N$ — $Ar_8$ — $N$ — $Ar_{10}$ - $Ar_2$ — $X_2$ 
 $Ar_7$   $Ar_9$ 

wherein  $X_1$  and  $X_2$  are the same or different polymerisable groups and wherein  $Ar_1$ ,  $Ar_2$ ,  $Ar_6$ ,  $Ar_7$ ,  $Ar_8$ ,  $Ar_9$ ,  $Ar_{10}$  are the same or different substituted or unsubstituted aryl or

3

heteroaryl groups. Examples of groups Ar<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>3</sub>, Ar<sub>4</sub>, Ar<sub>5</sub> Ar<sub>6</sub>, Ar<sub>7</sub>, Ar<sub>8</sub>, Ar<sub>9</sub>, and Ar<sub>10</sub> include such groups as phenylene, thiophene, pyrrole, furan, pyridine and biphenylene.

The aryl or heteroaryl groups Ar<sub>3</sub>, Ar<sub>4</sub>, Ar<sub>5</sub>, Ar<sub>6</sub>, Ar<sub>7</sub>, Ar<sub>8</sub>, Ar<sub>9</sub>, and Ar<sub>10</sub> may be substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl. Preferred substituents are butyl and *sec*-butyl.

Particularly preferred monomers according to the present invention include

wherein R and R' are selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl., preferably and R and R' are selected from the group comprising butyl and sec-butyl.

The present invention provides polymers obtainable by the polymerisation of the monomers of the present invention. The present invention also provides copolymers obtained by the polymerisation of monomers of the present invention with suitable comonomers, preferred comonomers are those selected from the group comprising fluorenes, benzothiadiazoles, phenylenes, triarylamines, quinoxalines and stilbenes, preferably said comonomers are fluorenes, benzothiadiazoles, phenylenes or triarylamines.

In a further embodiment the present invention provides an optoelectronic device comprising the polymers or copolymers of the present invention. In preferred embodiments said optoelectronic device is an electroluminescent device or a photovoltaic device.

The present invention provides a process for preparing the inventive polymers comprising polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and a monomer according to claim 1 having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX<sub>3</sub>-anionic groups, wherein X is independently selected from the group consisting of F and OH.

The present invention provides a process for preparing the inventive copolymers which comprises polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and one or more comonomers having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having at least two reactive halide functional groups, and one or more comonomers having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group; or at least (c) a monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group and one or more comonomers having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX3-anionic groups, wherein X is independently selected from the group consisting of F and OH.

# **Detailed Description of the Invention**

Monomers according to the invention can be prepared by any suitable route known to those skilled in the art. A preferred route involves Ullmann condensation to afford the amine units and Stille coupling to connect the amine units to further aryl or heteroaryl groups. An example of a typical synthetic route is shown

In the above scheme a triarylamine is formed by Ullmann condensation of a diamine and an aromatic iodide, this condensation is generally carried in an inert solvent in the presence of a catalyst such as copper powder, cuprous oxide, cuprous chloride, cuprous bromide, cuprous iodide or cuprous sulfate, 1,10-phenanthroline is added to expedite the reaction. Stille coupling is a common method of coupling aromatic units to heteroaromatic units, in the above scheme the electrophile substituted triarylamine is reacted with an organotin reagent in the presence of a palladium catalyst. Modifications of both Ullmann condensation and Stille coupling are well known to those in the art.

Examples of monomers according to the present invention include those having the following structural formulae

$$X_1 - X_2 - X_1 - X_1 - X_2 - X_1 - X_2 - X_1 - X_2 - X_1 - X_2 - X_1 - X_1$$

Polymers and copolymers according to the present invention may be prepared by any suitable method known to those skilled in the art, such as Yamamoto or Suzuki coupling, Suzuki coupling is preferred. In the case of monomers with thiophene or pyrrole substituents polymers and copolymers may be prepared by electrochemical polymerisation. Generally, in order to prepare a polymer by Suzuki coupling a suitably substituted monomer is polymerised in a solvent in the presence of a catalyst and a base. Suitable monomers are those comprising, for example, one polymerisable Br moiety and one polymerisable boronic ester moiety, alternatively the reaction mixture may comprise two monomers, one having, for example Br substituents and the other

having, for example, boronic ester substituents. The catalyst is a palladium catalyst such as tetrakis(triphenylphosphine)palladium, suitable bases include alkali or alkaline earth carbonates and alkali or alkaline earth bicarbonates or organic bases such as those disclosed in WO00/53656. The solvent is preferably one in which the polymer is soluble, for example suitable solvents include anisole, benzene, ethylbenzene, mesitylene, xylene and toluene. A typical reaction scheme for Suzuki polymerisation is shown below.

Similarly copolymers according to the present invention may be prepared by Yamamoto or Suzuki coupling, Suzuki coupling is preferred. Generally, in order to prepare a copolymer by Suzuki coupling suitably substituted monomers are polymerised in a solvent in the presence of a catalyst. Suitable reactants for the preparation of a two component copolymer are monomers having at least two boronic ester groups and second monomers having at least two Br groups alternatively monomers having one Br group and one boronic ester group and second monomers having one Br group and one

boronic ester group. Clearly terpolymers and higher copolymers could be prepared by reacting suitable monomers. The catalyst is a palladium catalyst such as tetrakis(triphenylphosphine)palladium, suitable bases include alkaline earth carbonates and alkaline earth bicarbonates or organic bases such as those disclosed in WO00/53656. The solvent is preferably one in which the polymer is soluble, for example suitable solvents for polyfluorenes include anisole, benzene, ethylbenzene, mesitylene, xylene and toluene.

End-capping reagents may be added to terminate the reaction or may be added after termination of the reaction. Examples of suitable end-capping reagents include phenylboronate and bromobenzene.

Examples of comonomers which may be compolymerised with the monomers of the present invention to form copolymers include the following, wherein  $X_1$  and  $X_2$  are polymerisable groups.

$$X_1$$
 $X_2$ 
 $X_1$ 
 $X_2$ 
 $X_1$ 
 $X_2$ 
 $X_3$ 
 $X_4$ 
 $X_4$ 

Examples of polymers and copolymers include those having the following structural formulae, wherein x, y and z represent the proportion of monomers in the copolymer.

The polymers and copolymers of the present invention may be used in optoelectronic devices such as electroluminescent devices and photovoltaic devices. An electroluminescent device according to the present invention typically comprises, on a suitable substrate, an anode, a cathode and a layer of light-emitting material positioned between the anode and the cathode. Electroluminescent devices may further comprise charge transport layers and/or charge injecting layers positioned between the light-emitting material and the anode or cathode as appropriate. In electroluminescent devices of the present invention the polymers or copolymers of the present invention may be present either as the light-emitting layer or as charge transporting or charge injecting layers or alternatively as charge transporting components in a blend with a light emitting material or as light emitting components in a blend with a charge transporting material. The thickness of the emitting layer can be in the range 10nm-300nm, preferably 50nm-200nm. In particular the polymers and copolymers of the present invention may act as hole-transporting layers or as hole-transporting components in a blend.

The anode of the device preferably comprises a material of high work function deposited on a substrate. Preferably the material has a work function greater than 4.3eV, examples of such materials include indium-tin oxide (ITO), tin oxide (TO), aluminum or indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide and metals such as Au, Ag, Ni, Pd and Pt. Suitable substrates include glass and plastics, the substrate may be rigid or flexible, transparent or opaque. The material of high work function is suitably deposited on the substrate to form a film of 50nm to 200nm, preferably said film has a sheet resistance of 10-100 Ohm/square, more preferably less than 30 Ohm/square.

The cathode of the device is preferably a material of low work function, preferably of work function less than 3.5eV. Examples of such materials include Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba, Yb, Sm and Al. The cathode may comprise an alloy of such metals or an alloy of such metals in combination with other metals, for example the alloys MgAg and LiAl. The cathode preferably comprises multiple layers, for example Ca/Al or LiAl/Al. The device may further comprise a layer of dielectric material between the cathode and the emitting layer, such as is disclosed in WO 97/42666. In particular it is preferred to use an

alkali or alkaline earth metal fluoride as a dielectric layer between the cathode and the emitting material. A particularly preferred cathode comprises LiF/Ca/Al, with a layer of LiF of thickness from 1 to 10nm, a layer of Ca of thickness of 1 to 25nm and a layer of Al of thickness 10 to 500nm.

Where the electroluminescent device comprises further charge injecting or charge transporting materials, these further materials may be present as separate layers or in a blend with the light emitting material. Examples of suitable charge transporting materials include polystyrene sulfonic acid doped polyethylene dioxythiophene (PEDOT-PSS), polyaniline with anionic dopants such as polymeric anionic dopants, and triarylamines, including polymeric triarylamines such as poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) BFA. The charge transport or charge injecting layers suitably have a thickness in the range 10nm to 200nm, preferably 1nm to 50nm.

A preferred structure of an electroluminescent device comprises a glass substrate, an ITO anode, a charge transporting layer of PEDOT-PSS, a layer of light-emitting material, a thin layer of LiF and a cathode comprising a layer of calcium and a layer of aluminum.

A photovoltaic device according to the present invention typically comprises two electrodes and situated between said two electrodes at least two semiconductive polymers having different electron affinities, one of said semiconductive polymers being a polymer according to the present invention. The semiconductive polymers may be in the form of a blend or may form separate layers, preferably said semiconductive polymers are in the form of a blend. Generally one of the electrodes comprises a material of high work function, such as ITO, other examples of suitable high work function materials are given above. Generally the other electrode comprises a material of low work function such as AI, other examples of suitable low work function materials are given above. Photovoltaic devices may comprise further charge injection and/or charge transport layers as appropriate, for example a layer of PEDOT/PSS may be included between the anode and the polymeric layer to aid hole transport and injection. Examples of such photovoltaic devices are disclosed in WO99/49525 and US5670791.

Polymers according to the present invention may also be used as the active component in photodetectors and photoconductors. In a photodetector the polymer is comprised in a layer of organic material situated between two electrodes, a voltage is applied across the layer of organic material and a current detecting circuit is used to measure the current generated due to incident light falling on the organic material. A photoconductor comprising a polymer of the present invention operates along similar lines but comprises a circuit to measure the change in resistance across the polymer layer which occurs when the device is exposed to light. Photodiodes and photodetectors are disclosed in WO99/09603, GB2315594 and US5523555.

## **EXAMPLES**

## **Synthesis of Trimer Precursor**

To a solution of 2-tributyl stannyl thiophene (10.16 mL, 17.56 mmol), Amine 2 (7.18 g, 13.3 mmol) in toluene (80 mL) was added tetrakis (triphenylphosphine)palladium(0) (731 mg). The reaction mixture was refluxed for 4 hours and then the heat removed. The suspension was filtered through celite and evaporated to dryness. Recrystallisation from hexane afforded 3.98g (56%yield) of desired product. A further 1.16g was obtained from the mother liquor. Overall yield (73%). Structure was confirmed by GC-MS and <sup>1</sup>H NMR.

## **Synthesis of dibromo Trimer**

To a solution of trimer precursor (3.97 g, 17.47 mmol) in DMF (40 mL) was added a solution of N-bromo succinimide (NBS) (2.66g, 14.94 mmol) in DMF (10 mL). The reaction mixture was stirred at room temperature for 30 mins. Monitored by GC-MS. A further 2.66g of NBS was added, this gave 100% of desired product by GC-MS. The reaction quenched by pouring the reaction mixture onto ice/ethanol. The product was filtered off and recrystallised from diethyl ether/ hexane affording, 5.19g (98% yield) of desired product.

# Polymerisation of AB copolymer F8Trimer:

To a solution of 9,9-di-n-octylfluorene-2,7-di(ethyleneborate) (F8), (0.9267g, 1.75 mmol) and dibromo trimer (1.2290g, 1.75 mmol) in toluene (5 mL) was added dichlorobis(triphenylphosphine) palladium (II) 4mg in toluene (2.55 mL). The solution was degassed for 10 min then tetraethyl ammonium hydroxide (5.82 mL) was added. The reaction mixture was heated to 115 °C for 19h. End capping reagents were then added as follows, 0.3ml bromobenzene was added and allowed to react for 1 hour at a temperature of 115°C, then 0.3g phenylboronic acid was added and allowed to react for 1 hour at a temperature of 115°C. The reaction mixture was allowed to cool to room temperature and poured into 0.5l methanol. The polymer was obtained as a precipitate. 1.14g of polymer of mass 15K was obtained.

The present invention is described with reference to a number of specific embodiments, it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

#### Claims

1. Monomer having the formula

 $X_1$ -Ar<sub>1</sub>-[triarylamine]-Ar<sub>2</sub>- $X_2$ 

wherein the triarylamine unit comprises at least one nitrogen atom in the backbone of the monomer and at least three substituted or unsubstituted aryl or heteroaryl groups, said groups being the same or different,

wherein  $X_1$  and  $X_2$  are the same or different polymerisable groups,

wherein  $Ar_1$  and  $Ar_2$  are the same or different substituted or unsubstituted aryl or heteroaryl groups.

- 2. Monomer according to claim 1 wherein Ar<sub>1</sub> and Ar<sub>2</sub> are heteroaryl groups.
- 3. Monomer according to claim 2 wherein Ar<sub>1</sub> and Ar<sub>2</sub> are selected from the group comprising benzene, thiophene, pyrrole, furan and pyridine.
- 4. Monomer according to claim 1 wherein X<sub>1</sub> and X<sub>2</sub> are the same or different and are selected from the group comprising Cl, Br, I, boronic acids, boronic esters and boranes.
- 5. Monomer according to claim 4 wherein  $X_1$  and  $X_2$  are the same or different and are selected from the group comprising Br and boronic esters.
- Monomer according to claim 1 wherein the triarylamine group comprises at least one heteroaryl group.
- Monomer according to claim 6 wherein the triarylamine group comprises a triazine group.

8. Monomer according to claim 1 wherein Ar<sub>1</sub> and Ar<sub>2</sub> are the same or different aryl or heteroaryl groups and are substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.

- 9. Monomer according to claim 1 wherein the triarylamine comprises one nitrogen atom.
- 10. Monomer according to claim 1 wherein the triarylamine comprises two nitrogen atoms.
- 11. Monomer according to claim 9 having the structure

$$X_1$$
— $Ar_1$ — $Ar_3$ — $N$ — $Ar_5$ — $Ar_2$ — $X_2$ 
 $Ar_4$ 

wherein X<sub>1</sub> and X<sub>2</sub> are the same or different polymerisable groups,

wherein  $Ar_1$ ,  $Ar_2$ ,  $Ar_3$ ,  $Ar_4$  and  $Ar_5$  are the same or different substituted or unsubstituted aryl or heteroaryl groups.

- 12. Monomer according to claim 11 wherein groups Ar<sub>3</sub>, Ar<sub>4</sub> and Ar<sub>5</sub> are substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.
- 13. Monomer according to claim 10 having the structure

$$X_1$$
— $Ar_1$ — $Ar_6$ — $N$ — $Ar_8$ — $N$ — $Ar_{10}$ - $Ar_2$ — $X_2$ 
 $Ar_7$   $Ar_9$ 

wherein  $X_1$  and  $X_2$  are the same or different polymerisable groups,

wherein  $Ar_1$ ,  $Ar_2$ ,  $Ar_6$ ,  $Ar_7$ ,  $Ar_8$ ,  $Ar_9$ ,  $Ar_{10}$  are the same or different substituted or unsubstituted aryl or heteroaryl groups.

- 14. Monomer according to claim 13 wherein groups Ar<sub>6</sub>, Ar<sub>7</sub>, Ar<sub>8</sub>, Ar<sub>9</sub>, Ar<sub>10</sub> are substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.
- 15. Monomers according to claim 1 having the structures

wherein R and R' are selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.

- 16. Polymer obtainable by the polymerisation of a monomer according to claim 1.
- 17. Copolymer obtainable by the polymerisation of a monomer according to claim 1 and one or more comonomers.
- 18. Copolymer according to claim 17 obtainable by the copolymerisation of a monomer according to claim 1 and one or more comonomers selected from the group comprising fluorenes, benzothiadiazoles, phenylenes, triarylamines, stilbenes, quinoxalines, and biphenylenes.

19. Copolymer according to claim 18 obtainable by the copolymerisation of a monomer according to claim 1 and a comonomer selected from the group comprising fluorenes, benzothiadiazoles, triarylamines and phenylenes.

- Optoelectronic device comprising a polymer according to claim 16 or a copolymer according to claim 17.
- 21. Optoelectronic device according to claim 20 wherein said device is an electroluminescent device.
- 22. Optoelectronic device according to claim 20 wherein said device is a photovoltaic device.
- 23. A process for preparing a polymer according to claim 16, which comprises polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and a monomer according to claim 1 having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX3-anionic groups, wherein X is independently selected from the group consisting of F and OH.
- 24. A process for preparing a copolymer according to claim 17, which comprises polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and one or more comonomers having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having at least two reactive halide functional groups, and one or more comonomers having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group; or at least (c) a

monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group and one or more comonomers having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX3-anionic groups, wherein X is independently selected from the group consisting of F and OH.

## INTERNATIONAL SEARCH REPORT

Int ional Application No PCT/GB 02/04723

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G61/12 C07D333/20										
According to International Patent Classification (IPC) or to both national classification and IPC										
B. FIELDS	SEARCHED currentation searched (classification system followed by classification	n sambols)								
IPC 7	COSG CO7D	ii ayiiiboa)								
Documentat	Ion searched other than minimum documentation to the extent that su	ch documents are included in the fields sea	arched							
	ata base consulted during the international search (name of data base									
EPO-In	ternal, WPI Data, BEILSTEIN Data, CH	EM ABS Data								
C DOCUM	ENTS CONSIDERED TO BE RELEVANT									
Category °	Cliation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No.							
Category	Ollaholi ol document, with indicators, which appropriate, or the rot	, , , , , , , , , , , , , , , , , ,								
Α	WO 01 66618 A (TOWNS CARL ROBERT		1-24							
	RICHARD O (GB); CAMBRIDGE DISPLAY (GB) 13 September 2001 (2001-09-1									
	page 1; claim 1; examples 2-7	3)								
	NAME OF THE PARTY	*	1-24							
А	WO 01 44769 A (SWANTECH L L C) 21 June 2001 (2001-06-21)		1-24							
	cited in the application	,								
	page 1; claims 1,6,10; example 3									
A	WO 01 49768 A (TOWNS CARL ROBERT		1-24							
	RICHARD O (GB); CAMBRIDGE DISPLAY	TECH								
	(GB) 12 July 2001 (2001-07-12) cited in the application									
	page 1; claim 22									
	·									
			7							
Furt	her documents are listed in the continuation of box C.	X Patent family members are listed	in annex.							
° Special ca	ategories of cited documents :	*T* later document published after the Inte	rnational filing date							
"A" docum	ent defining the general state of the art which is not dered to be of particular relevance	or priority date and not in conflict with cited to understand the principle or the invention	eory underlying the							
	document but published on or after the international	"X" document of particular relevance; the c cannot be considered novel or cannot	laimed invention be considered to							
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another "Y" document of particular relevance; the claimed invention										
citation or other special reason (as specified)  cannot be considered to involve an inventive step when the document is combined with one or more other such docu-										
other	means ent published prior to the international filing date but	ments, such combination being obvior in the art.								
later t	han the priority date claimed actual completion of the International search	*&* document member of the same patent family  Date of mailing of the international search report								
Date of the	वनक्व क्याफ़िलामा व एक पारमाचाणाच २००८।									
9	January 2003	20/01/2003								
Name and	mailing address of the ISA	Authorized officer								
	European Patent Office, P.B. 5818 Patentiaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,	01								
	Fax: (+31-70) 340-3016	Seelmann, I								

## INTERNATIONAL SEARCH REPORT

nformation on patent family members

int onal Application No PCT/GB 02/04723

	nt document search report		Publication date		Patent family member(s)		Publication date
WO O	166618	A	13-09-2001	AU	238500	1 A	16-07-2001
				ΑU	376180	1 A	17-09-2001
				EP	1246860	0 A1	09-10-2002
				EP	1263837	7 A1	11-12-2002
				WO	0149769	9 A1	12-07-2001
				WO	0166618	8 A1	13-09-2001
				AU	269000	1 A	16-07-2001
				AU	317770	0 A	04-10-2000
				AU	357730	1 A	03-09-2001
				AU	357780	1 A	03-09-2001
				EP	116974		09-01-2002
				EP	124472		02-10-2002
				EP	126383		11-12-2002
				EP	125761		20-11-2002
				WO	014976		12-07-2001
				MO	016282		30-08-2001
				WO	016286	9 A1	30-08-2001
WO O	144769	Α	21-06-2001	US	635171	3 B1	26-02-2002
	_ , , , , ,			EP	125057	7 A1	23-10-2002
				МО	014476	9 A1	21-06-2001
WO O	149768	Α	12-07-2001	AU	269000	1 A	16-07-2001
				EP	124472	3 A2	02-10-2002
				WO	014976	8 A2	12-07-2001
				AU	317770		04-10-2000
				AU	357730	1 A	03-09-2001
				AU	357780		03-09-2001
				AU	376180		17-09-2001
				EP	116974		09-01-2002
				EP	126383		11-12-2002
				EP	125761		20-11-2002
				EP	126383		11-12-2002
				WO	016282		30-08-2001
				WO	016286		30-08-2001 13-09-2001
				WO	016661	A 87	1 2002001